

THE ELECTRONIC SPECTRA OF SOME TRISUBSTITUTED BENZENES IN DIFFERENT STATES. II

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ABSTRACT. The near ultraviolet absorption spectra of 1,2,4-trimethylbenzene and 3,4-dichlorotoluene have been investigated in different states. In the case of these two 1,2,4-trisubstituted benzenes, the allowed transition is of type $A'-A'$ and the 0,0 bands appear strongly in the spectra of the substances in the vapour state, but the spectrum of each of the compounds in the solid state at -180°C is very weak compared to the spectra due to the vapour and liquid states. The 0,0 band at -180°C is also displaced towards high energy region with respect to its position in the case of the liquid. It is suggested that the observed bands may represent only one of the two components into which the bands are split up in the crystals at -180°C .

It has been pointed out that the interaction of permanent dipoles of neighbouring molecules on the transition moment of the molecules in the lattice might be partly responsible for this large splitting.

INTRODUCTION

The ultraviolet absorption spectra of some trisubstituted benzene compounds have recently been investigated in this laboratory to study the influence of intermolecular forces on the position and structure of absorption bands in the liquid and solid states. Recently, it has been proposed by Sirkar (1962, 63) that the interaction of permanent electric moments of the neighbouring molecules on the transition moments of the molecules in the lattice might be partly responsible for the large splitting observed in the spectra of some crystals of polar molecules at -180°C .

In a previous communication (Misra, 1963) it has been pointed out that in 1, 2, 3-trisubstituted benzenes, the transition which is forbidden in free molecules due to cancellation of three migrational moment vectors, becomes allowed at -180°C , but no large splitting of bands could be detected. Since the magnitude of transition moment is very small in these cases, the interaction with the permanent dipoles of neighbouring molecules is expected to be weak. It was therefore, thought worthwhile to extend the investigation to some other polar molecules having a large value of transition moment and 1, 2, 4-trimethylbenzene and 3, 4-dichlorotoluene were selected for the purpose.

EXPERIMENTAL

The experimental set up was the same as described in an earlier paper (Misra 1960). Chemically pure samples of 1, 2, 4-trimethylbenzene and 3, 4-dichlorotoluene supplied by Eastman Kodak Co., and Fisher Scientific Co., U.S.A. respectively were used after fractional and repeated vacuum distillation. For studying the absorption spectrum of 3, 4-dichlorotoluene in the vapour state, a 75 cm long absorption tube provided with quartz windows and a bulb attached to a side tube for containing the liquid was used.

Thin films of the substances of thickness of the order of a few microns were used to produce bands in the liquid and solid states. The spectrograms were taken on Agfa Isopan films with a Hilger E 1 spectrograph having a dispersion of about 3 Å per mm. in the 2600 Å region. Microphotometric records were taken with a Kipp and Zonen type Moll microphotometer and absorption spectra were calibrated with the help of a microphotometric record of iron arc spectrum photographed on each spectrogram as explained in a previous paper (Sirkar and Misra, 1959).

RESULTS AND DISCUSSION

The microphotometric records of the absorption spectra of 1, 2, 4-trimethylbenzene and 3, 4-dichlorotoluene are reproduced in Figs. 1 and 2. The wave numbers of the bands with their approximate intensities and probable assignments are given in Tables I and II respectively.

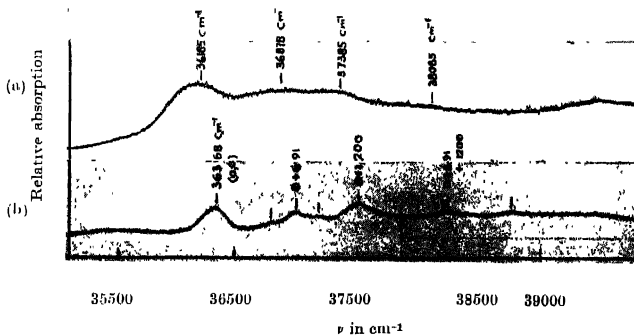


Fig. 1. Microphotometric records of the ultraviolet absorption spectra of 1,2,4-trimethylbenzene in different states.

- (a) In the liquid states at 32°C.
- (b) In the solid states at -180°C.

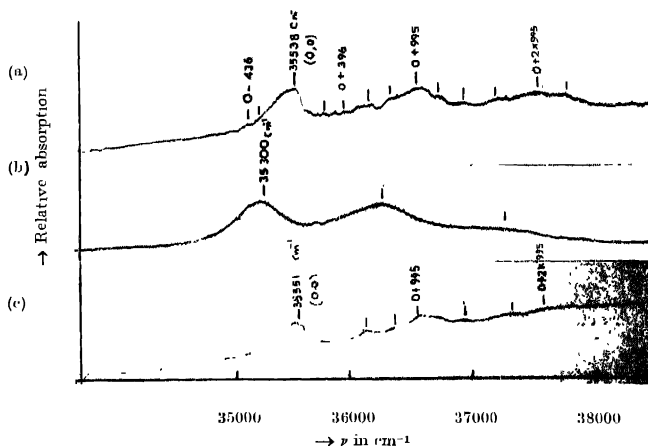


Fig. 2. Microphotometric records of the ultraviolet absorption spectra of 3, 4-dichlorotoluene in different states
(a) Vapour state. (b) Liquid state at 22°C (c) Solid state at - 180°C.

1, 2, 4-Trimethylbenzene

The near ultraviolet absorption spectrum of 1, 2, 4-trimethyl benzene in the vapour state was studied by Sreeramamurty (1951). Assuming the methyl group to behave as a single atom, this molecule has the lowest symmetry (C_s) among the substituted benzenes and the A_{1g} B_{2u} transition in benzene becomes $A'-A'$ transition in this case. This transition is an allowed one and the 0,0 band appears strongly in the spectrum. The data for the spectrum in the vapour state as reported by Sreeramamurty (1951) have been included in the table for comparison.

In the vapour state, the spectrum of 1, 2, 4-trimethylbenzene (Sreeramamurty, 1951) shows a strong 0,0 bands at 36900 cm^{-1} and a large number of bands involving different vibrational frequencies. In the liquid state, the compound yields four broad bands with the positions of maximum absorption at 36185, 36878, 37385 and 38085 cm^{-1} respectively (Fig. 1, Table I). The bands due to the liquid are broad probably due to thermal motion of molecules and merging of $v \rightarrow v'$ transitions into one another. The approximate position of the centre of the strong band on the long wavelength side at 36185 cm^{-1} is taken as the position of the 0, 0 band. Then it is found that on liquefaction of the vapour, the 0, 0 band shifts towards red by 715 cm^{-1} . The other bands are at distances 693, 1200 and 1900 cm^{-1} respectively from the 0,0 band.

With the solidification of the liquid and cooling to -180°C , some more bands are observed. The strongest band on the long wavelength side is at 36368 cm^{-1} and is taken as the 0,0 band of the system. The other bands can then be represented by excited state vibrational frequencies 461, 691, 890 and 1200 cm^{-1} and their combinations. Some of these frequencies agree fairly well with the frequencies 711, 927 and 1180 cm^{-1} reported by Sreeramamurty for the vapour state. The frequency 641 cm^{-1} observed in the spectrum of the crystals

TABLE I

Ultraviolet absorption bands of 1, 2, 4-trimethylbenzene in different states

Vapour (Sreeramamurty, 1951)		Liquid at 32°C		Solid at -180°C	
Wave number (cm^{-1}) and Intensity	Assignment	Wave number (cm^{-1}) and Intensity	Assignment	Wave number (cm^{-1}) and Intensity	Assignment
35977 (vw)	0 - 923				
36351 (vw)	0 - 549				
36683 (vw)	0 - 217				
36900 (vs)	0,0	36185 (s)	0,0	36368 (vs)	0,0
37015 (m)	0 115			36824 (w)	0 + 461
37611 (s)	0 711	36878 (s)	0 693	37059 (s)	0 + 691
37827 (ms)	0 927	37385 (s)	0 1200	37258 (m)	0 + 890
38080 (mw)	0 + 1180			37568 (s)	0 + 1200
		38085 (m)	0 693 + 1200		
38186 (mw)	0 1286			38268 (m)	0 + 691 + 1200
				38760 (w)	0 + 2 \times 1200

at -180°C was not observed by him in the case of the vapour, but it may be noted that Kohlrausch and Pongratz (Magat, 1936) reported two strong Raman lines 557 cm^{-1} and 474 cm^{-1} . It is seen that when the vapour is liquefied the band system shifts towards red by 715 cm^{-1} and on solidification and subsequent cooling to -180°C , the band system shifts towards shorter wavelength by 183 cm^{-1} . Further, the integrated absorption at each band becomes much smaller when the liquid is frozen and cooled to -180°C .

This decrease in the strength of absorption may be explained by assuming that this band system constitutes one of the two components in which the original band system is split up in the crystal at -180°C and that the other component may be on the short wavelength side. As the crystal structure of the compound

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at -180°C is not known it has not been possible to calculate the exact positions of the split components.

3, 4-Dichlorotoluene

As explained above this molecule also has the symmetry C_s and the migrational moment vectors add to give a large value. The transition is allowed and the 0,0 band is expected to appear strongly in the spectrum of free molecules.

Spectrum in the vapour phase.

Three groups of bands degraded towards red, consisting of about fifteen prominent bands (Fig. 2a) have been observed. The very strong sharp band at 35538 cm^{-1} on the long wavelength side has been taken as the 0,0 band of the system. All the other bands can then be assigned in terms of ground state frequencies 363 and 436 cm^{-1} and upper state fundamentals 232, 396, 598, 799, 995, and 1170 their combinations.

TABLE II

Ultraviolet absorption bands of 3, 4-dichlorotoluene in different states

Vapour at 32°C Path length 75 cm		Liquid at 32°C		Solid at -180°C	
Wave number (cm^{-1}) and Intensity	Assignment	Wave number (cm^{-1}) and Intensity	Assignment	Wave number (cm^{-1}) and Intensity	Assignment
35102 (w)	0 - 436				
35175 (w)	0 - 363				
35538 (vs)	0,0	35300 (vs)	0,0	35551 (vs)	0,0
35770 (w)	0 + 232	36292 (vs)	0 + 992	36123 (m)	0 + 572
35934 (w)	0 + 396	37284 (m)	0 + 2×992	36347 (w)	0 + 796
36136 (m)	0 + 598			36546 (s)	0 + 995
36317 (m)	0 + 779			36930 (w)	0 + 572 + 796
	0 + 2×396				
				37302 (m)	0 + 995 + 796
36533 (vs)	0 + 995				
36718 (ms)	0 + 1170			37554 (m)	0 + 2×995
36925 (m)					
	0 + 995 + 396				
	0 + 598 + 779				
37163 (ms)	0 + 1625				
	0 + 995 + 598				
37529 (s)	0 + 2×995				
37767 (ms)	0 + 2×995 + 232				

The Raman and infrared spectra of the molecule have recently been reported by Deb and Banerjee (1960). The two ground state fundamentals 363 and 436 cm^{-1} observed as $\nu \rightarrow 0$ transition in the present investigation agrees with the Raman frequencies 368 and 435 cm^{-1} reported by them. The upper state fundamentals 396, 598, 779, 995 and 1170 cm^{-1} satisfactorily correspond to the Raman and infrared frequencies 435, 686, 805, 1030 and 1211 cm^{-1} reported by Deb and Banerjee (1960).

In the liquid state, the substance gives a spectrum consisting of three broad bands. The centres of the first band at 35300 cm^{-1} is taken as the position of the 0, 0 band and other bands are separated from it by 992 cm^{-1} and 2×992 cm^{-1} . Thus on liquefaction of the vapour the band system is shifted towards red by 238 cm^{-1} .

In the solid state at -180°C , the absorption spectrum of the substance consists of about seven prominent but weak bands. The first band at 35551 cm^{-1} is evidently the 0, 0 band of the system. The other bands can then be explained in terms of upper state fundamentals 572, 796 and 995 cm^{-1} . Thus on solidification of the vapour and its subsequent cooling to -180°C , the band system is observed to shift slightly towards higher energies and also the strength of absorption diminishes appreciably.

This decrease in the strength of absorption in the crystals at -180°C may be explained in the same way as in the previous case. It may be noted here that similar shift of one of the split components to the other region of the spectrum has also been observed by Bornstein in the case of bromobenzene as reported by Kasha and Oppenheimer (1962).

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